Convenient Routes to Vinylideneruthenium Dichlorides with Basic and Bulky Tertiary Phosphine Ligands (PPr^i_3 and PCy_3)

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Two synthetic routes to vinylideneruthenium complexes bearing basic and bulky tertiary phosphine ligands, $RuCl_2\{=C=C(E)R\}L_2$ [L = PPr^i_3, E = H, R = Ph (**3a**), *t*-Bu (**3b**), ferrocenyl (**3c**), *p*-$MeO_2CC_6H_4$ (**3d**), *p*-$MeOC_6H_4$ (**3e**); L = PCy_3, E = H, R = Ph (**4a**), *t*-Bu (**4b**), ferrocenyl (**4c**); L = PPr^i_3, E = $SiMe_3$, R = Ph (**6**), 1,1′-ferrocenediyl (**7**)], have been developed. Treatment of Ru(methallyl)$_2$(cod) (**1**) with PPr^i_3 and HCl (each 2 equiv) at −20 °C provides $[RuCl_2(PPr^i_3)_2]_n$, which instantly reacts with phenylacetylene and *tert*-butylacetylene at room temperature to give **3a**,**b** in isolated yields of 61 and 57%, respectively. On the other hand, heating a toluene solution of $[RuCl_2(p\text{-cymene})]_2$ (**2**), phosphine (2 equiv/Ru), and alkyne (1 equiv/Ru) at 80 °C leads to the selective formation of the corresponding vinylidene complex. A variety of complexes (**3a**−**e**, **4a**−**c**, **6**, **7**) are prepared from terminal alkynes and (trimethylsilyl)acetylene derivatives in 97−52% isolated yields. Treatment of **2** with PPr^i_3 (2 equiv/Ru) and MeCN (10 equiv/Ru) in toluene gives $RuCl_2(PPr^i_3)_2(NCMe)_2$ (**5**) in 75% yield, which also serves as the precursor for vinylidene complexes. The X-ray crystal structures of **3a**, **4a**, and **5** are reported.

Introduction

A great deal of attention has been focused on ring-opening metathesis polymerization (ROMP) of cyclic olefins catalyzed by well-defined transition metal complexes.[1,2] We have recently found that vinylideneruthenium dichlorides bearing PPr^i_3 or PCy_3 ligands, $RuCl_2\{=C=C(H)Bu^t\}L_2$ (L = PPr^i_3, PCy_3), serve as good catalyst-precursors for ROMP of norbornene derivatives.[3,4] Although efficiency of the vinylidene complexes as the initiator is much lower than that of the well-known Grubbs' alkylidene complexes, the polymerization rate is rapid enough for practical use and the resulting polymers have high molecular weights with polydispersity equivalent to the alkylidene systems.[5] In addition, the vinylidene precursors have an advantage that they may be readily prepared from conventional terminal alkynes. However, this system has still suffered from the lack of general synthetic routes to the vinylidene complexes bearing basic and bulky tertiary phosphine ligands. Thus, while the PPr^i_3 and PCy_3 complexes can be synthesized by ligand substitution of the PPh_3 analogues,[6] their isolated yields are restricted to 20−30% due to difficulty in separating the complexes from PPh_3 liberated in the systems.[3a]

One of the most convenient methods of synthesizing vinylideneruthenium of the form $RuCl_2\{=C=C(H)R\}L_2$ so far reported is the treatment of $RuCl_2L_n$ complexes with terminal alkynes, which was first demonstrated in 1991 by Wakatsuki et al. using $RuCl_2(PPh_3)_3$.[6] Despite intensive studies on transition metal vinylidene complexes in recent years,[7] this method has never been applied to the other phosphine systems, probably due to the lack of practical routes to dichlororuthenium precursors other than $RuCl_2(PPh_3)_3$. Recently, Werner et al. employed $RuH_2Cl_2(PPr^i_3)_2$, which is prepared from $[RuCl_2(cod)]_n$ and H_2 (1.5 bar) in butanol at 80 °C, as the starting material for $RuCl_2\{=C=C(H)Ph\}(PPr^i_3)_2$.[8] Grubbs et al. reported the synthesis of $RuCl_2(=C=CH_2)$-

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(2) (a) Lynn, D. M.; Mohr, B.; Grubbs, R. H. *J. Am. Chem. Soc.* **1998**, *120*, 1627−1628. (b) Maughon, B. R.; Grubbs, R. H. *Macromolecules* **1997**, *30*, 3459−3469. (c) Schwab, P.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1996**, *118*, 100−110. (d) Nguyen, S.-B. T.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1993**, *115*, 9858−9859. (e) Mashima, K.; Tanaka, Y.; Kaidzu, M.; Nakamura, A. *Organometallics* **1996**, *15*, 2431−2433.

(3) (a) Katayama, H.; Ozawa, F. *Chem. Lett.* **1998**, 67−68. (b) Katayama, H.; Yoshida, T.; Ozawa, F. *J. Organomet. Chem.* **1998**, *562*, 203−206.

(4) Catalytic activity for ROMP of the vinylideneruthenium $RuCl_2(=C=CH_2)(PCy_3)_2$ was reported.[2c]

(5) In our preliminary work,[3a] the polydispersity of poly(norbornene) ranging from 2.6 to 4.1 was found with 10 mM of catalyst-precursors. The value has been improved to 1.3−1.5 by lowering the concentration of catalyst-precursors to 2.0 mM: Katayama, H.; Ozawa, F. Unpublished result.

(6) Wakatsuki, Y.; Koga, N.; Yamazaki, H.; Morokuma, K. *J. Am. Chem. Soc.* **1994**, *116*, 8105−8111.

(7) For leading references, see: (a) Slugovc, C.; Mereiter, K.; Schmid, R.; Kirchner, K. *J. Am. Chem. Soc.* **1998**, *120*, 6175−6176. (b) Takagi, Y.; Matsuzaka, H.; Ishii, Y.; Hidai, M. *Organometallics* **1997**, *16*, 4445−4452. (c) Bourgault, M.; Castillo, A.; Esteruelas, M. A.; Oñate, E.; Ruiz, N. *Organometallics* **1997**, *16*, 636−645. (d) Werner, H.; Lass, R. W.; Gevert, O.; Wolf, J. *Organometallics* **1997**, *16*, 4077−4088. (e) O'Connor, J. M.; Hiibner, K.; Merwin, R.; Gantzel, P. K.; Fong, B. S. *J. Am. Chem. Soc.* **1997**, *119*, 9, 3631−3632.

(8) Grünwald, C.; Gevert, O.; Wolf, J.; González-Herrero, P.; Werner, H. *Organometallics* **1996**, *15*, 1960−1962.

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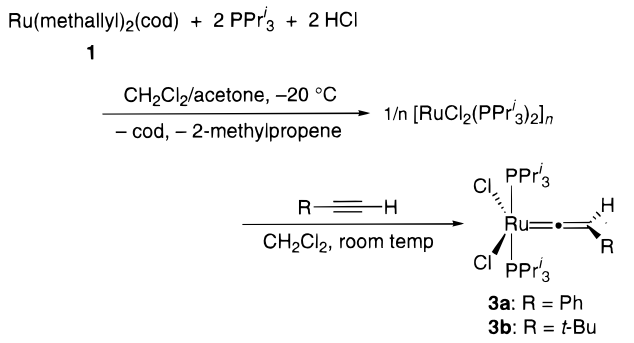
Scheme 1



$(PCy_3)_2$ by the reaction of $RuCl_2\{=C(H)Ph\}(PCy_3)_2$ with 1,2-propadiene.[2c] We herein report more simple ways to vinylideneruthenium complexes bearing PPr^i_3 and PCy_3 ligands which utilize common ruthenium complexes, Ru(methallyl)$_2$(cod) (**1**)[9] and $[RuCl_2(p\text{-cymene})]_2$ (**2**),[10] as the starting materials.

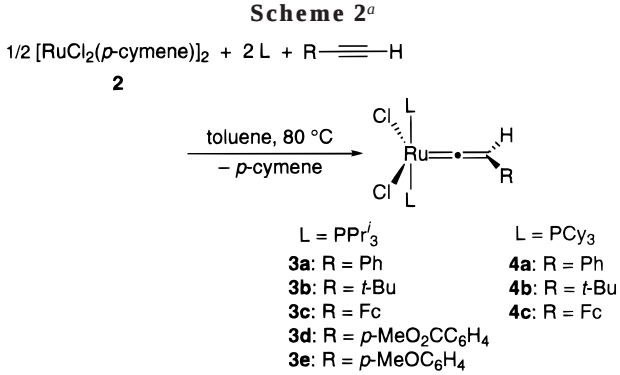
Results and Discussion

Synthesis from Ru(methallyl)$_2$(cod) (1). This route is based on the synthesis of $RuBr_2$(P*P) (P*P = chiral bidentate phosphines), reported by Genet and coworkers.[9] Complex **1** was dissolved in a mixture of CH_2Cl_2 and acetone and treated successively with PPr^i_3 and dry HCl in MeOH (each 2 equiv) at −20 °C (Scheme 1). The initially colorless solution instantly turned yellow, and a pale yellow crystalline solid was gradually precipitated from the solution over 30 min. The ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR data and the low solubility of the precipitate in common organic solvents such as CH_2Cl_2 and acetone suggested the formation of $[RuCl_2(PPr^i_3)_2]_n$ with an oligomeric structure. Since this complex was thermally unstable in solution as well as in the solid state, the reactions with alkynes were conducted without isolation.

Terminal alkynes (10 equiv/**1**) were added to the above reaction mixture. On being stirred at room temperature, the initially heterogeneous systems gradually turned to deep purple solutions. ^{31}P{^{1}H} NMR spectroscopy revealed the formation of vinylidene complexes in 70−80% selectivities. Complexes **3a**[11] and **3b** were isolated in 61 and 57% yields by this route.

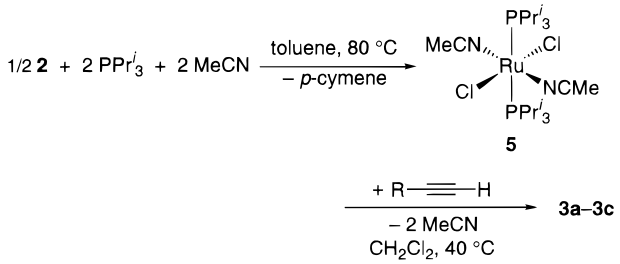
Synthesis from $[RuCl_2(p\text{-cymene})]_2$ (2). The vinylidene complexes **3a**−**e** and **4a**−**c** listed in Scheme 2 were synthesized more readily from **2**.[10] When a mixture of **2**, PPr^i_3 (2 equiv/Ru), and PhC≡CH (1 equiv/Ru) in toluene was heated at 80 °C, the initially reddish brown solution gradually darkened. ^{31}P{^{1}H} NMR spectroscopy revealed the formation of $RuCl_2$(*p*-cymene)-(PPr^i_3) (δ 41.5)[12] at the initial stage, which was successively converted to $RuCl_2\{=C=C(H)Ph\}(PPr^i_3)_2$ (**3a**) (δ 29.5) over 26 h. Complex **3a** was isolated in 97% yield as an analytically pure compound by removal of volatile materials from the reaction system, followed by washing the crude product with MeOH. Similarly, the PPr^i_3 complexes **3b**−**e** were prepared in isolated yields of 96−52%. The PCy_3 complexes **4a**−**c** were synthesized by this route and isolated as crystals simply by cooling the reaction solutions. Attempts to prepare PBu^t_3-coordinated vinylidene complexes were unsuccessful.

Scheme 2[a]



[a] Fc = ferrocenyl.

Scheme 3



The reaction of **2** with PPr^i_3 (2 equiv/Ru) in toluene in the absence of terminal alkynes gave a complex mixture. In the presence of acetonitrile (10 equiv/Ru), on the other hand, the same reaction provided $RuCl_2$-$(PPr^i_3)_2(NCMe)_2$ (**5**)[13] in 75% isolated yield, which was found to serve as a good precursor for vinylidene complexes (Scheme 3). The IR spectrum of **5** exhibited a strong absorption peak at 2265 cm^{-1}, assignable to the ν_{CN} band. The appearance of only one ν_{CN} band is consistent with the mutually trans arrangement of the MeCN ligands. The ^{1}H NMR spectrum showed one set of signals arising from the PPr^i_3 ligands (δ 2.87 (m), 1.41 (doublet of virtual triplets)) and a triplet of the MeCN protons (δ 2.37, $^5J_{PH}$ = 1.2 Hz). Furthermore, only a singlet at δ 21.9 was observed in the ^{31}P{^{1}H} NMR spectrum. These NMR observations indicate the mutually trans coordination of the two PPr^i_3 ligands. Hence the all trans geometry around the ruthenium is evidenced.

Figure 1 shows the X-ray structure of **5**. The ruthenium atom has typical octahedral geometry. The MeCN ligands bound to ruthenium are slightly bending to avoid steric repulsion to one of the *i*-Pr groups of the phosphine ligand (∠Ru−N−C(1) = 175.6(2)°, ∠N−C(1)−C(2) = 178.2(2)). The N−C(1) and C(1)−C(2) distances (1.146(3) and 1.456(3) Å) are in the typical range of a

(9) (a) Genet, J. P.; Pinel, C.; Ratovelomanana-Vidal, V.; Mallart, S.; Pfister, X.; Caño de Andrade, M. C.; Laffitte, J. A. *Tetrahedron*: *Asymmetry* **1994**, *5*, 665−674. (b) Genet, J. P.; Pinel, C.; Ratovelomanana-Vidal, V.; Mallart, S.; Pfister, X.; Bischoff, L.; Caño de Andrade, M. C.; Darses, S.; Galopin, C.; Laffitte, J. A. *Tetrahedron*: *Asymmetry* **1994**, *5*, 675−690. (c) Genet, J. P.; Mallart, S.; Pinel, C.; Jugé, S. *Tetrahedron*: *Asymmetry* **1991**, *2*, 43−46. Complex **1** is commercially available from Janssen Chimica.

(10) Bennett, M. A.; Smith, A. K. *J. Chem. Soc., Dalton Trans.* **1974**, 233−241.

(11) Complex **3a** was recently prepared by another route.[8]

(12) Serron, S. A.; Nolan, S. P. *Organometallics* **1995**, *14*, 4611−4616.

(13) A related compound $RuCl_2(PPh_3)_2(NCMe)_2$ was reported: Cole-Hamilton, D. J.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1979**, 1283−1289.

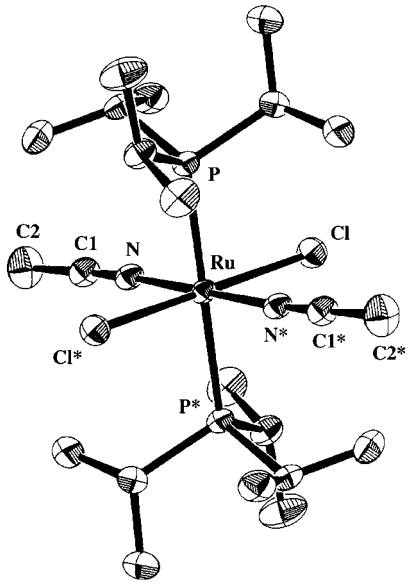


Figure 1. ORTEP diagram of $RuCl_2(PPr^i_3)_2(NCMe)_2$ (**5**) showing 50% probability thermal ellipsoids. Selected bond distances (Å) and angles (deg): Ru−Cl = 2.4324(5), Ru−P = 2.4305(6), Ru−N = 2.010(2), N−C(1) = 1.146(3), C(1)−C(2) = 1.456(3), Cl−Ru−Cl* = 180.00, P−Ru−P* = 180.00, N−Ru−N* = 180.00, Cl−Ru−P = 89.96(2), Cl−Ru−N = 87.56(5), P−Ru−N = 88.24(5), Ru−N−C(1) = 175.6(2), N−C(1)−C(2) = 178.2(2).

Table 1. Selected Bond Distances (Å) and Angles (deg) and Dihedral Angles between Least-Squares Planes (deg) for 3a and 4a

	3a	4a
Ru−C(1)	1.750(4)	1.761(2)
Ru−Cl(1)	2.338(1)	2.3668(7)
Ru−Cl(2)	2.3541(9)	2.3623(7)
Ru−P(1)	2.421(1)	2.4241(6)
Ru−P(2)	2.424(1)	2.4080(6)
C(1)−C(2)	1.329(5)	1.334(3)
Ru−C(1)−C(2)	177.1(3)	178.5(2)
Cl(1)−Ru−Cl(2)	158.63(4)	156.93(2)
P(1)−Ru−P(2)	169.17(3)	170.94(2)
(Ru, Cl(1), Cl(2), C(1)) vs (C(1), C(2), C(3))	1.40	6.99

nitrogen−carbon triple bond and of a carbon−carbon single bond, respectively.

The reaction of **5** with phenylacetylene (1 equiv) in CH_2Cl_2 was complete within 20 h at 40 °C to give the vinylidene complex **3a** in quantitative yield (NMR). Complexes **3b**,**c** were similarly prepared using *tert*-butylacetylene and ferrocenylacetylene, respectively.

Characterization of Vinylidene Complexes. Vinylidene complexes thus prepared were characterized by elemental analysis and ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy. The data for **3a** were in fair agreement with those reported.[8] The other vinylidene complexes exhibited $^{13}C\{^1H\}$ NMR signals characteristic of the α- and β-vinylidene carbons (δ 337.1−344.6 and 103.2−115.5, respectively).

The structures of vinylidene complexes **3a** and **4a** were determined by single-crystal X-ray diffraction studies. The selected bond distances and angles are listed in Table 1. As seen from the ORTEP drawings in Figures 2 and 3, both complexes have a distorted square pyramidal structure having the vinylidene ligand

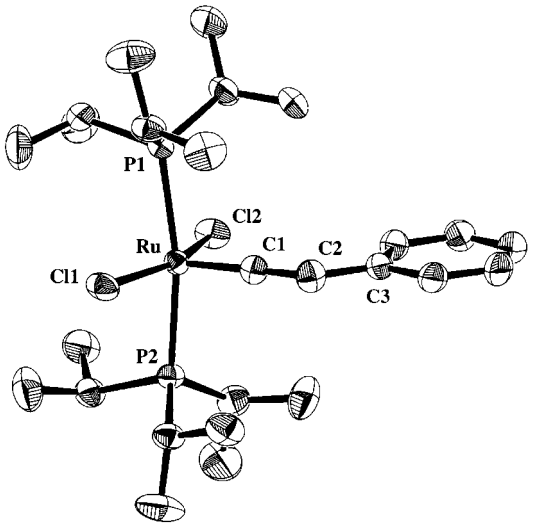


Figure 2. ORTEP diagram of $RuCl_2\{=C=C(H)Ph\}(PPr^i_3)_2$ (**3a**) showing 30% probability thermal ellipsoids. Only one of the two essentially superposable but crystallographically independent molecules is shown.

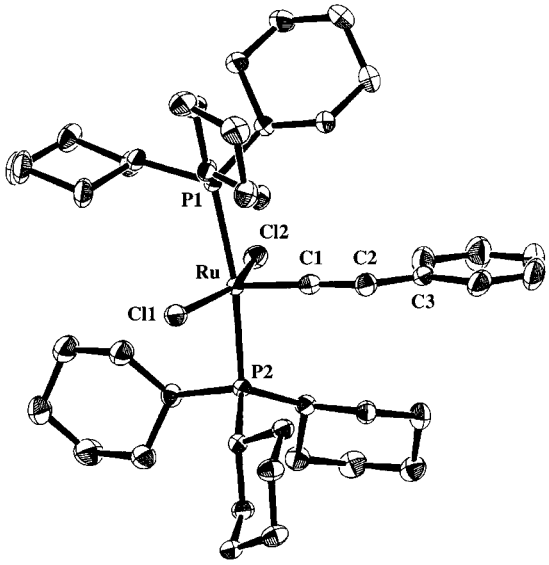
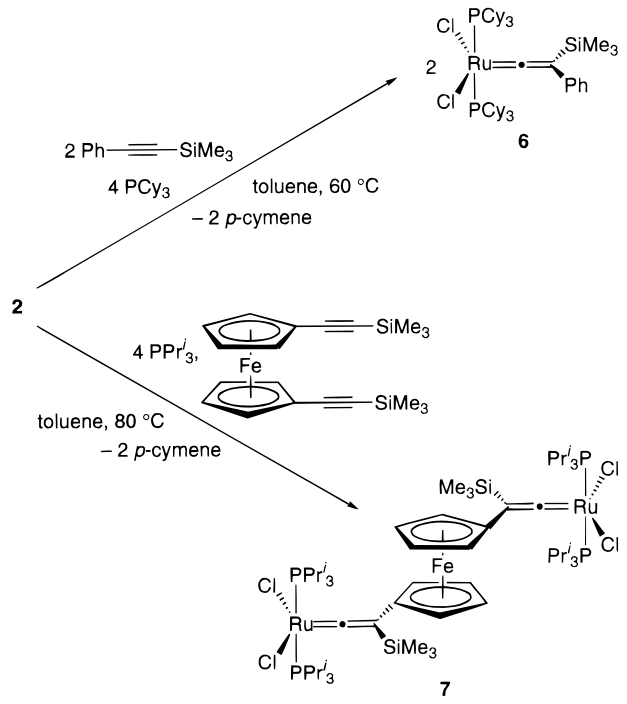


Figure 3. ORTEP diagram of $RuCl_2\{=C=C(H)Ph\}(PCy_3)_2 \cdot CH_2Cl_2$ (**4a**) showing 50% probability thermal ellipsoids. The solvent molecule is omitted for clarity.

at the apical position. The Ru−C(1)−C(2) angles are almost linear (177.1(3) for **3a**; 178.5(2)° for **4a**), and the Cl(1)−Ru−Cl(2) and P(1)−Ru−P(2) axes are bent away from the vinylidene ligand (158.63(4) and 156.93(2)° for **3a**; 169.17(3) and 170.94(2)° for **4a**). The Ru−C(1) distances (1.750(4) for **3a**; 1.761(2) Å for **4a**) are comparable to each other and to that of $RuBr_2\{=C=C(H)Bu^t\}(PPh_3)_2$ (1.768(17) Å)[6] but shorter than those of the coordinatively saturated vinylideneruthenium complexes $[CpRu\{=C=C(Me)Ph\}(PPh_3)_2]^+I^-$ (1.863(10) Å),[14] $[RuCl\{=C=C(H)Ph\}(\kappa^2(P,O)\text{-}Pr^i_2PCH_2CH_2\text{-}OMe)_2]^+OTf^-$ (1.790(3) Å),[15] and $TpRuCl\{=C=C(H)Ph\}(PPh_3)$ (1.801(4) Å),[16] probably reflecting the apical arrangement of the vinylidene ligands without trans

(14) Bruce, M. I.; Humphrey, M. G.; Snow, M. R.; Tiekink, E. R. T. *J. Organomet. Chem.* **1986**, *314*, 213−225.
(15) Martín, M.; Gevert, O.; Werner, H. *J. Chem. Soc., Dalton Trans.* **1996**, 2275−2283.

Scheme 4



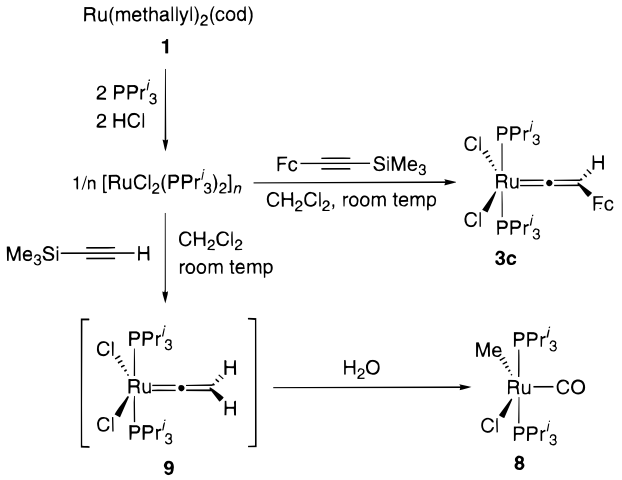
donor ligand. The vinylidene groups lie approximately on the least-squares plane composed of the Ru, Cl(1), Cl(2), and C(1) atoms. A similar structural feature has been observed for the alkylidene complex $RuCl_2\{=CH(C_6H_4Cl\text{-}p)\}(PCy_3)_2$.[2c]

Synthesis of *β*-Silylvinylidene Complexes. The present routes could be applied to the synthesis of *β*-silylvinylidene complexes via 1,2-silyl migration of silylacetylenes (Scheme 4).[17] The reaction of **2**, PCy_3 (2 equiv/Ru), and $PhC{\equiv}CSiMe_3$ (10 equiv/Ru) in toluene at 60 °C for 51 h gave $RuCl_2\{=C=C(SiMe_3)Ph\}(PCy_3)_2$ (**6**). The $^{13}C\{^1H\}$ NMR spectrum exhibited characteristic signals assignable to the α- and *β*-vinylidene carbons at *δ* 330.1 (t, $^2J_{PC}$ = 12 Hz) and 108.2 (br s), respectively. The methyl protons and carbons of the $SiMe_3$ group were observed at *δ* 0.29 (s) and 1.88 (s) in the ^1H and $^{13}C\{^1H\}$ NMR spectra, respectively.

When 1,1′-bis{(trimethylsilyl)ethynyl}ferrocene (1 equiv/**2**) was employed as the starting silylacetylene, a ferrocene derivative with two (*β*-silylvinylidene)ruthenium units (**7**) was obtained in 92% yield. The composition was confirmed by elemental analysis. The C_2-symmetrical structure was suggested by NMR spectroscopy, where a set of signals similar to $RuCl_2\{=C=C(H)Fc\}(PPr^i_3)$ (**3c**, Fc = ferrocenyl) was observed.

Synthesis of *β*-silylvinylidene complexes was also examined with **1** as the starting material (Scheme 5). Treatment of $[RuCl_2(PPr^i_3)_2]_n$, in situ generated from **1**, with $FcC{\equiv}CSiMe_3$ did not afford the expected *β*-silylvinylidene complex but the desilation product **3c** in 67% selectivity (NMR). The reaction with $Me_3SiC{\equiv}CH$ gave a complex mixture of ruthenium species, from which $RuMeCl(CO)(PPr^i_3)_2$ (**8**) was isolated in 15% yield. Complex **8** exhibited a strong ν_{CO} band at 1893 cm^{-1} in the IR spectrum. In the $^{13}C\{^1H\}$ NMR spectrum, signals assignable to the carbonyl and methyl carbons were observed at *δ* 202.0 (t, $^2J_{PC}$ = 14 Hz) and −13.4 (t, $^2J_{PC}$ = 7 Hz), respectively.

Scheme 5[a]



[a] Fc = ferrocenyl.

In both reactions in Scheme 5, the formation of Me_3SiOH was observed by GC-MS spectrometry. Since the parent silylacetylenes are stable to desilation under the reaction conditions and desilation was observed only in the reactions in Scheme 5 (i.e., not in the reactions in Scheme 4), *β*-silylvinylidene complexes generated from $[RuCl_2(PPr^i_3)_2]_n$ and silylacetylenes are considered to undergo desilation with the aid of residual water and HCl in the systems. Actually, isolated **6** was found to be readily converted into the desilation product **4a** at room temperature in CH_2Cl_2 in the presence of a small amount of dilute hydrochloric acid. The formation of methyl carbonyl complex **8** may be rationalized as follows. Nucleophilic attack of water on the α-vinylidene carbon of the nonsubstituted vinylidene complex **9**, probably with the aid of HCl catalyst, followed by enol to keto tautomerization of the resulting hydroxycarbene complex leads to a 14-electron acetylruthenium species, which subsequently undergoes decarbonylation to give **8**. This type of transformation has already been documented.[18]

Experimental Section

General Procedure and Materials. All manipulations were performed under an argon atmosphere using conventional Schlenk techniques or in a nitrogen-filled glovebox. Argon gas was purified by passage through P_2O_5 (Merck, SICAPENT). ^1H, ^{13}C, and ^{31}P NMR spectra were recorded on a JEOL JNM-A400 or a Varian Mercury 300 spectrometer. Chemical shifts are reported in *δ* (ppm), referenced to the ^1H (of residual protons) and ^{13}C signals of deuterated solvents or

(16) Slugovc, C.; Mereiter, K.; Zobetz, E.; Schmid, R.; Kirchner, K. *Organometallics* **1996**, *15*, 5275−5277.

(17) For precedents of transition metal-promoted 1,2-silyl migration of silylacetylenes to give *β*-silylvinylidene complexes, see: (a) Werner, H.; Baum M.; Schneider, D.; Windmüller, B. *Organometallics* **1994**, *13*, 1089−1097. (b) Katayama, H.; Onitsuka, K.; Ozawa, F. *Organometallics* **1996**, *15*, 4642−4645. (c) Connelly, N. G.; Geiger, W. E.; Lagunas, M. C.; Metz, B.; Rieger, A. L.; Rieger, P. H.; Shaw, M. J. *J. Am. Chem. Soc.* **1995**, *117*, 12202−12208. (d) Sakurai, H.; Fujii, T.; Sakamoto, K. *Chem. Lett.* **1992**, 339−342. (e) Naka, A.; Okazaki, S.; Hayashi, M.; Ishikawa, M. *J. Organomet. Chem.* **1995**, *499*, 35−41.

(18) (a) de los Ríos, I.; Jiménez, T.; Puerta, C.; Valerga, P. *J. Am. Chem. Soc.* **1997**, *119*, 6529−6538. (b) Gamasa, M. P.; Gimeno, J.; Lastra, E.; Lanfranchi, M.; Tiripicchio, A. *J. Organomet. Chem.* **1992**, *430*, C39−C43. (c) Bruce, M. I.; Swincer, A. G. *Aust. J. Chem.* **1980**, *33*, 1471−1483.

to the ^{31}P signal of external 85% H_3PO_4. Infrared spectra were recorded at room temperature on a JASCO FT/IR-410 instrument.

Toluene, benzene, THF, and hexane were dried over sodium benzophenone ketyl. Methanol was dried with $Mg(OMe)_2$. CH_2Cl_2 and acetonitrile were dried over CaH_2. These solvents were distilled and stored over activated molecular sieves (MS4A) under an argon atmosphere. $CDCl_3$, CD_2Cl_2, and benzene-d_6 were dried over MS4A, vacuum transferred, and stored under a nitrogen atmosphere in the dark. Ru(methallyl)$_2$(cod),[9] [$RuCl_2$(*p*-cymene)]$_2$,[10] PPr^i_3,[19] ferrocenylacetylene,[20] *p*-$MeO_2CC_6H_4C{\equiv}CH$,[21] *p*-$MeOC_6H_4C{\equiv}CH$,[21] and 1,1′-bis{(trimethylsilyl)ethynyl}ferrocene[20] were prepared according to the literature. Liquid alkynes were degassed by three freeze−pump−thaw cycles prior to use. All other compounds were obtained from commercial sources and used without purification.

Synthesis of Vinylidene Complexes 3a−e and 4a−c. (a) From Ru(methallyl)$_2$(cod) (1). To a colorless solution of **1** (202 mg, 0.632 mmol) in CH_2Cl_2 (25 mL) and acetone (16 mL) was added PPr^i_3 (201 mg, 1.25 mmol) at room temperature. The mixture was cooled to −20 °C, and a solution of HCl in MeOH (1.7 M, 0.74 mL, 1.3 mmol) was added dropwise. The solution instantly turned yellow, and then a yellow precipitate gradually formed from the solution. After the mixture was stirred for 30 min at −20 °C, the precipitate was collected by filtration, washed with cold pentane, and dried under vacuum at low temperature (<−20 °C). Since the product was thermally unstable, its elemental analysis was infeasible, but the NMR data clearly indicated the formation of [$RuCl_2(PPr^i_3)_2$]$_n$. ^1H NMR (CD_2Cl_2, −30 °C): δ 2.82−2.70 (m, 6H, PC*H*CH_3), 1.45 (dd, $^2J_{PH}$ = 16.8 Hz, $^3J_{HH}$ = 7.1 Hz, 36H, PCHC*H*$_3$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −30 °C): δ 19.0 (d, $^1J_{PC}$ = 40 Hz, P*C*HCH$_3$), 17.7 (s, PCH*C*H$_3$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −30 °C): δ 35.6 (s).

The reactions with alkynes were performed without isolation of [$RuCl_2(PPr^i_3)_2$]$_n$. To a suspension of [$RuCl_2(PPr^i_3)_2$]$_n$, which was prepared from **1** (248 mg, 0.777 mmol), PPr^i_3 (249 mg, 1.55 mmol), and a MeOH solution of HCl (1.7 M, 0.94 mL, 1.6 mmol) in CH_2Cl_2 (30 mL) and acetone (20 mL), was added PhC≡CH (0.80 g, 7.8 mmol) in one portion at −20 °C. On being stirred at room temperature, the heterogeneous mixture gradually turned to a deep purple homogeneous solution. After 16 h, the solution was concentrated to dryness by pumping, and the resulting solid was washed with MeOH (6 mL × 3) at −20 °C to give a brown microcrystalline solid of **3a** (279 mg, 61%). The NMR data were identical with those reported.[8] Similarly, **3b** was obtained with *tert*-butylacetylene in place of phenylacetylene in 57% yield.

(b) From [$RuCl_2$(*p*-cymene)]$_2$ (2). A typical procedure is as follows. To a suspension of **2** (205 mg, 0.335 mmol) in toluene (11 mL) was added PPr^i_3 (214 mg, 1.34 mmol) with stirring at room temperature. The mixture instantly changed into a reddish brown solution. PhC≡CH (68 mg, 0.67 mmol) was added, and the solution was heated at 80 °C for 26 h with stirring. The solution gradually darkened. Volatile materials were thoroughly removed by pumping, and the resulting oily product was washed with MeOH (2 mL × 3) at −70 °C to give a brown microcrystalline solid of **3a** (386 mg, 97%), which was analytically pure. All complexes listed in Scheme 2 were similarly prepared. Complex **3b** was prepared using an excess amount (10 equiv/Ru) of *t*-BuC≡CH; otherwise the yield considerably lowered. Complexes **4a−c** could be isolated as crystals simply by cooling the reaction solutions at −20 °C overnight. Complexes **3a−e** could be crystallized by slow diffusion of MeOH into CH_2Cl_2 solutions at −20 °C.

$RuCl_2${=C=C(H)Bu^t}(PPr^i_3)$_2$ (3b): brown solid (57%, from **1**; 96%, from **2**); ^1H NMR ($CDCl_3$, 23 °C) δ 3.06 (t, $^4J_{PH}$ = 3.6 Hz, 1H, =C=CH), 2.97−2.85 (m, 6H, PC*H*CH$_3$), 1.40 (doublet of virtual triplets, $^3J_{HH}$ = 5.8 Hz, J = 6.6 Hz,[22] 36H, PCHC*H*$_3$), 1.10 (s, 9H, *t*-Bu); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 23 °C) δ 337.1 (t, $^2J_{PC}$ = 15 Hz, Ru=*C*=C), 115.5 (t, $^3J_{PC}$ = 5 Hz, Ru=C=*C*), 32.1 (s, C(*C*H$_3$)$_3$), 23.1 (virtual triplet, J = 9 Hz,[22] P*C*HCH$_3$), 20.1 (s, PCH*C*H$_3$); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 23 °C) δ 27.1 (s). Anal. Calcd for $C_{24}H_{52}Cl_2P_2Ru$: C, 50.17; H, 9.12. Found: C, 49.96; H, 9.08.

$RuCl_2${=C=C(H)Fc}(PPr^i_3)$_2$ (3c): brown solid (67% from **2**); ^1H NMR ($CDCl_3$, 23 °C) δ 4.16 (t, $^4J_{PH}$ = 3.3 Hz, 1H, =C=CH), 4.06 (s, 5H, C_5H_5), 4.04, 3.92 (each apparent triplet, J = 1.8 Hz, 2H, C_5H_4), 2.90−2.78 (m, 6H, PC*H*CH$_3$), 1.36 (doublet of virtual triplets, $^3J_{HH}$ = 6.0 Hz, J = 7.1 Hz,[22] 36H, PCHC*H*$_3$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 23 °C) δ 338.6 (t, $^2J_{PC}$ = 15 Hz, Ru=*C*=C), 103.2 (t, $^3J_{PC}$ = 4 Hz, Ru=C=*C*), 78.6 (s, C^1 of C_5H_4), 68.7 (s, C_5H_5), 66.9, 66.2 (each s, C_5H_4), 23.2 (virtual triplet, J = 9 Hz,[22] P*C*HCH$_3$), 20.1 (s, PCH*C*H$_3$); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 23 °C) δ 29.8 (s). Anal. Calcd for $C_{30}H_{52}Cl_2P_2FeRu$: C, 51.29; H, 7.46. Found: C, 51.19; H, 7.46.

$RuCl_2${=C=C(H)$C_6H_4CO_2$Me-*p*}(PPr^i_3)$_2$ (3d): brown solid (52% from **2**). An analytically pure compound containing 1 equiv of CH_2Cl_2 in the crystal was obtained by recrystallization from CH_2Cl_2/MeOH (18% yield). IR (KBr): 1716 ($\nu_{C=O}$), 1580 ($\nu_{C=C}$) cm^{-1}. ^1H NMR (C_6D_6, 19 °C): δ 8.15, 7.17 (each d, J = 8.8 Hz, 2H, C_6H_4), 4.69 (t, $^4J_{PH}$ = 3.4 Hz, 1H, =C=CH), 4.24 (s, 2H, CH_2Cl_2), 3.48 (s, 3H, CO_2CH_3), 2.80−2.68 (m, 6H, PC*H*CH$_3$), 1.25 (doublet of virtual triplets, $^3J_{HH}$ = 6.4 Hz, J = 6.4 Hz,[22] 36H, PCHC*H*$_3$). $^{13}C\{^1H\}$ NMR (C_6D_6, 19 °C): δ 338.0 (t, $^2J_{PC}$ = 15 Hz, Ru=*C*=C), 166.7 (s, *C*O_2CH$_3$), 140.1 (s, C^4 of C_6H_4), 130.2 (s, $C^{3,5}$ of C_6H_4), 126.1 (s, C^1 of C_6H_4), 124.8 (s, $C^{2,6}$ of C_6H_4), 108.8 (t, $^3J_{PC}$ = 5 Hz, Ru=C=*C*), 53.0 (s, CH_2Cl_2), 51.2 (s, CO_2CH_3), 23.7 (virtual triplet, J = 9 Hz,[22] P*C*HCH$_3$), 20.0 (s, PCH*C*H$_3$). $^{31}P\{^1H\}$ NMR (C_6D_6, 19 °C): δ 30.3 (s). Anal. Calcd for $C_{28}H_{50}Cl_2O_2P_2Ru{\cdot}CH_2Cl_2$: C, 47.23; H, 7.11. Found: C, 47.83; H, 7.18.

$RuCl_2${=C=C(H)C_6H_4OMe-*p*}(PPr^i_3)$_2$ (3e): dark green solid (63% from **2**); ^1H NMR ($CDCl_3$, 19 °C): δ 6.89, 6.73 (each d, J = 8.8 Hz, 2H, C_6H_4), 4.50 (t, $^4J_{PH}$ = 3.4 Hz, 1H, =C=CH), 3.75 (s, 3H, OCH_3), 2.90−2.81 (m, 6H, PC*H*CH$_3$), 1.35 (doublet of virtual triplets, $^3J_{HH}$ = 6.4 Hz, J = 6.6 Hz,[22] 36H, PCHC*H*$_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 19 °C) δ 344.6 (t, $^2J_{PC}$ = 15 Hz, Ru=*C*=C), 156.4 (s, C^4 of C_6H_4), 126.1 (s, $C^{3,5}$ of C_6H_4), 124.4 (s, C^1 of C_6H_4), 113.6 (s, $C^{2,6}$ of C_6H_4), 108.2 (t, $^3J_{PC}$ = 5 Hz, Ru=C=*C*), 55.2 (s, OCH_3), 23.3 (virtual triplet, J = 8 Hz,[22] P*C*HCH$_3$), 20.0 (s, PCH*C*H$_3$); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 19 °C) δ 28.7 (s). Anal. Calcd for $C_{27}H_{50}Cl_2OP_2Ru$: C, 51.92; H, 8.07. Found: C, 51.98; H, 8.11.

$RuCl_2${=C=C(H)Ph}(PCy_3)$_2$ (4a): dark purple solid (87% from **2**); ^1H NMR (C_6D_6, 60 °C) δ 7.18−7.09, 7.03−6.98, 6.89−6.84 (each m, 5H, Ph), 4.70 (t, $^4J_{PH}$ = 3.6 Hz, 1H, =C=CH), 2.88−2.75, 2.30−2.15, 1.82−1.50, 1.30−1.08 (each m, 66H, Cy); $^{13}C\{^1H\}$ NMR (C_6D_6, 60 °C) δ 342.1 (t, $^2J_{PC}$ = 14 Hz, Ru=*C*=C), 133.9 (s, C^1 of Ph), 128.5, 125.8, 124.1 (each s, C^{2-6} of Ph), 109.6 (t, $^3J_{PC}$ = 5 Hz, Ru=C=*C*), 34.0 (virtual triplet, J = 8 Hz,[22] C^1 of Cy), 30.7 (s, $C^{3,5}$ of Cy), 28.3 (s, $C^{2,6}$ of Cy), 27.0 (s, C^4 of Cy); $^{31}P\{^1H\}$ NMR (C_6D_6, 60 °C) δ 22.5 (s). Anal. Calcd for $C_{44}H_{72}Cl_2P_2Ru$; C, 63.29; H, 8.69. Found; C, 63.49; H, 8.42.

$RuCl_2${=C=C(H)Bu^t}(PCy_3)$_2$ (4b): purple solid (63% from **2**); ^1H NMR ($CDCl_3$, 20 °C) δ 2.84 (t, $^4J_{PH}$ = 3.6 Hz, 1H, =C=CH), 2.70−2.56, 2.15−2.04, 1.88−1.56, 1.34−1.16 (each m, 66H, Cy), 1.07 (s, 9H, *t*-Bu); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 20 °C) δ 338.5 (t, $^2J_{PC}$ = 14 Hz, Ru=*C*=C), 114.7 (t, $^3J_{PC}$ = 5 Hz, Ru=C=*C*), 33.1 (virtual triplet, J = 9 Hz,[22] C^1 of Cy), 32.3 (s, *C*(CH$_3$)$_3$), 32.0 (s, $C^{3,5}$ of Cy), 30.1 (s, C(*C*H$_3$)$_3$), 27.9 (virtual

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(22) Apparent coupling constant for the virtual triplet signal.

Table 2. Crystallographic Data and Structure Refinement for 3a, 4a, and 5

	3a	4a	5
formula	$C_{26}H_{48}Cl_2P_2Ru$	$C_{44}H_{72}Cl_2P_2Ru\cdot CH_2Cl_2$	$C_{22}H_{48}N_2Cl_2P_2Ru$
fw	594.59	919.91	574.56
cryst size, mm	0.4 × 0.3 × 0.3	0.4 × 0.2 × 0.2	0.5 × 0.4 × 0.1
cryst syst	monoclinic	triclinic	monoclinic
space group	$P2_1/a$ (No. 14)	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)
a, Å	24.363(3)	13.923(2)	11.248(2)
b, Å	9.721(3)	14.353(2)	8.593(1)
c, Å	28.088(3)	13.168(3)	14.969(1)
α, deg		110.07(2)	
β, deg	115.660(6)	112.61(1)	104.250(8)
γ, deg		76.08(1)	
V, Å^3	5996(2)	2263.7(7)	1402.2(3)
Z	8	2	2
d_{calcd}, g cm^{-3}	1.317	1.350	1.361
μ(Mo Kα), cm^{-1}	8.20	6.83	8.75
F(000)	2496	972	604
2θ range, deg	5.0−55.0	5.0−55.0	5.0−55.0
temp, K	296	198	198
transm factors	0.96−1.00	0.92−1.00	0.80−1.00
no. of rflns collcd	14229	10808	3386
no. of unique rflns	13748 (R_{int} = 0.032)	10378 (R_{int} = 0.025)	3226 (R_{int} = 0.036)
no. of obsd rflns	8415 ($I \geq 3\sigma(I)$)	8556 ($I \geq 3\sigma(I)$)	2827 ($I \geq 3\sigma(I)$)
no. of variables	559	469	134
R^a	0.033	0.033	0.025
$R_w{}^b$	0.034	0.053	0.034
GOF^c	1.39	1.22	2.12
max Δ/σ in final cycle	0.06	0.00	0.01
max and min peak, e Å^{-3}	0.30, −0.33	1.15, −0.94	0.44, −0.65

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, $w = 1/[\sigma^2(F_o)]$. ^{c} GOF = $[\sum w(|F_o| - |F_c|)^2/(N_o - N_p)]^{1/2}$.

triplet, J = 5 Hz,[22] C^{2,6} of Cy), 26.7 (s, C^4 of Cy). ^{31}P{^{1}H} NMR ($CDCl_3$, 20 °C) δ 17.9 (s). Anal. Calcd for $C_{42}H_{76}Cl_2P_2Ru$: C, 61.90; H, 9.40. Found: C, 61.73; H, 9.29.

$RuCl_2${=C=C(H)Fc}$(PCy_3)_2$ (4c): deep purple solid (91% from **2**); ^{1}H NMR (C_6D_6, 17 °C) δ 4.25 (t, $^4J_{PH}$ = 3.2 Hz, 1H, =C=CH), 4.17 (s, 5H, C_5H_5), 4.09, 4.05 (each apparent triplet, J = 1.6 Hz, 2H, C_5H_4), 2.88−2.75, 2.30−2.16, 1.85−1.58, 1.35−1.15 (each m, 66H, Cy); ^{13}C{^{1}H} NMR (C_6D_6, 17 °C) δ 338.3 (t, $^2J_{PC}$ = 14 Hz, Ru=*C*=C), 103.3 (br, Ru=C=*C*), 79.2 (s, C^1 of C_5H_4), 69.2 (s, C_5H_5), 67.6, 66.8 (each s, C^{2,5} and C^{3,4} of C_5H_4), 33.5 (virtual triplet, J = 8 Hz,[22] C^1 of Cy), 30.6 (s, C^{3,5} of Cy), 28.2 (s, C^{2,6} of Cy), 26.9 (s, C^4 of Cy). ^{31}P{^{1}H} NMR (C_6D_6, 17 °C) δ 21.8 (s). Anal. Calcd for $C_{48}H_{76}Cl_2P_2FeRu\cdot 0.5C_7H_8$: C, 62.55; H, 8.15. Found: C, 62.48, H, 8.07.

Synthesis of $RuCl_2(PPr^i_3)_2(NCMe)_2$ (5). To a suspension of **2** (202 mg, 0.330 mmol) in toluene (11 mL) were added MeCN (0.34 mL, 6.5 mmol) and PPr^i_3 (212 mg, 1.32 mmol) at room temperature. The reaction mixture was stirred at 80 °C for 16 h. The initially reddish brown solution gradually turned heterogeneous to give orange precipitate of **5**, which was collected by filtration using a filter-paper-tipped cannula, washed with hexane (3 mL × 3), and dried under vacuum (283 mg, 75%). IR (KBr): 2265 (ν_{CN}) cm^{-1}. ^{1}H NMR ($CDCl_3$, 23 °C): δ 2.93−2.81 (m, 6H, PC*H*CH$_3$), 2.37 (virtual triplet, J = 1.2 Hz,[22] 6H, CH_3CN), 1.41 (doublet of virtual triplets, $^3J_{HH}$ = 6.3 Hz, J = 6.0 Hz,[22] 36H, PCHC*H*$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$, 23 °C): δ 124.9 (s, CH_3*C*N), 23.3 (virtual triplet, J = 8 Hz,[22] P*C*HCH$_3$), 19.8 (s, PCH*C*H$_3$), 5.5 (s, *C*H$_3$CN). ^{31}P{^{1}H} NMR ($CDCl_3$, 23 °C): δ 21.9 (s). Anal. Calcd for $C_{22}H_{48}N_2Cl_2P_2Ru$: C, 45.99; H, 8.42; N, 4.88. Found: C, 45.87; H, 8.40; N, 4.93.

Reaction of 5 with Alkynes. To a suspension of **5** (63 mg, 0.11 mmol) in CH_2Cl_2 (2.7 mL) was added PhC≡CH (12 mg, 0.12 mmol). The reaction mixture was stirred at 40 °C for 20 h. As the reaction proceeded the yellow suspension gradually turned to a dark purple solution. The resulting solution was concentrated to dryness by pumping. ^{1}H and ^{31}P{^{1}H} NMR analysis of the resulting solid revealed the selective formation of **3a**. The reactions of **5** with *tert*-butylacetylene and ferrocenylacetylene were similarly examined, where **3b**,**c** were formed in quantitative yields as confirmed by NMR spectroscopy.

Synthesis of $RuCl_2${=C=C(SiMe$_3$)Ph}$(PCy_3)_2$ (6). To a suspension of **2** (100 mg, 0.163 mmol) in toluene (5 mL) were added PCy_3 (185 mg, 0.659 mmol) and PhC≡CSiMe$_3$ (580 mg, 3.33 mmol) at room temperature. The mixture was stirred at 60 °C for 51 h. The initially deep purple solution gradually darkened. The resulting solution was allowed to stand at −30 °C for 1 day to give dark purple crystals of **6**, which was collected by filtration and dried under vacuum (90 mg). The filtrate was concentrated to dryness, and the resulting solid was recrystallized from CH_2Cl_2/MeOH to give second crop of **6** (88 mg; totally 60%). ^{1}H NMR ($CDCl_3$, 18 °C): δ 7.28−7.09, 6.90−6.85 (each m, 5H, Ph), 2.70−2.60, 2.10−2.08, 1.82−1.49, 1.30−1.10 (each m, 66H, Cy), 0.29 (s, 9H, SiMe$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$, 18 °C): δ 330.1 (t, $^2J_{PC}$ = 12 Hz, Ru=*C*=C), 135.8 (s, C^1 of Ph), 129.0, 128.2, 127.5 (each s, C$^{2-6}$ of Ph), 108.2 (br s, Ru=C=*C*), 33.0 (virtual triplet, J = 8 Hz,[22] C^1 of Cy), 30.1 (s, C^{3,5} of Cy), 27.9 (s, C^{2,6} of Cy), 26.6 (s, C^4 of Cy), 1.88 (s, SiMe$_3$). ^{31}P{^{1}H} NMR ($CDCl_3$, 18 °C): δ 20.6 (s). Anal. Calcd for $C_{47}H_{80}Cl_2P_2SiRu$: C, 62.23; H, 8.89. Found: C, 61.97; H, 8.78.

Synthesis of 7. To a suspension of **2** (204 mg, 0.333 mmol) in toluene (11 mL) were added PPr^i_3 (214 mg, 1.34 mmol) and 1,1′-bis{(trimethylsilyl)ethynyl}ferrocene (127 mg, 0.336 mmol) at room temperature. The mixture was stirred at 80 °C for 35 h. The initially reddish brown solution gradually turned dark purple. Volatile materials were removed by pumping, and the resulting solid was washed with MeOH (3 mL × 3) to give a dark purple microcrystalline solid of **7** (418 mg, 92%), which was spectroscopically pure. Analytically pure compound containing 1 equiv of CH_2Cl_2 in the crystal was obtained by recrystallization from CH_2Cl_2 (71% yield). ^{1}H NMR ($CDCl_3$, 19 °C): δ 5.30 (s, 2H, CH_2Cl_2), 4.02−3.88 (m, 8H, C_5H_4), 2.94−2.73 (m, 12H, PC*H*CH$_3$), 1.35 (doublet of virtual triplets, $^3J_{HH}$ = 6.4 Hz, J = 6.4 Hz,[22] 72H, PCHC*H*$_3$), 0.30 (s, 18H, SiMe$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$, 19 °C): δ 325.7 (t, $^2J_{PC}$ = 14 Hz, Ru=*C*=C), 102.9 (s, Ru=C=*C*), 84.2 (s, C^1 of C_5H_4), 68.4, 66.9 (each s, C^{2,5} and C^{3,4} of C_5H_4), 54.0 (s, CH_2Cl_2), 23.1 (virtual triplet, J = 9 Hz,[22] P*C*HCH$_3$), 20.3 (s, PCH*C*H$_3$), 2.5 (s, SiMe$_3$). ^{31}P{^{1}H} NMR ($CDCl_3$, 19 °C): δ 29.4 (s). Anal. Calcd for $C_{56}H_{110}Cl_4FeP_4Si_2Ru_2\cdot CH_2Cl_2$: C, 47.27; H, 7.79. Found: C, 47.27; H, 7.79.

Reaction of $[RuCl_2(PPr^i_3)_2]_n$ with FcC≡CSiMe$_3$. The precipitate of $[RuCl_2(PPr^i_3)_2]_n$, formed from **1** (23.3 mg, 72.9 μmol) in CH_2Cl_2 and acetone (vide supra), was filtered out, washed with cold pentane, and dried under vacuum. The complex was suspended in CH_2Cl_2 (2 mL) at −20 °C, and FcC≡CSiMe$_3$ (207 mg, 0.732 mmol) was added. The mixture was stirred at room temperature for 4 h. GC-MS analysis of the dark orange solution showed the formation of Me_3SiOH. The solution was concentrated to dryness by pumping to give a dark brown solid. The ^{1}H and ^{31}P{^{1}H} NMR spectra indicated the formation of **3c** in 67% selectivity, along with some unidentified ruthenium species.

Reaction of $[RuCl_2(PPr^i_3)_2]_n$ with Me$_3$SiC≡CH. The complex $[RuCl_2(PPr^i_3)_2]_n$ prepared from **1** (201 mg, 0.629 mmol) similarly to the above experiment was suspended in CH_2Cl_2 (16 mL) at −20 °C, and $Me_3SiC{\equiv}CH$ (0.62 g, 6.3 mmol) was added in one potion. The mixture was stirred at room temperature for 30 min. The dark purple solution was concentrated to dryness by pumping, and the resulting solid was recrystallized from CH_2Cl_2/MeOH to give deep red crystals of $RuMeCl(CO)(PPr^i_3)_2$ (**8**) (47 mg, 15%). The product was spectroscopically pure, but did not provide satisfactory elemental analysis. IR (KBr): 1893 (ν_{CO}) cm^{-1}. ^{1}H NMR ($CDCl_3$, 23 °C): δ 2.79−2.67 (m, 6H, PC*H*CH$_3$), 1.28 (doublet of virtual triplets, $^3J_{HH}$ = 7.1 Hz, J = 13.2 Hz,[22] 36H, PCHC*H*$_3$), 1.19 (t, $^3J_{HP}$ = 4.9 Hz, 3H, RuCH$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$, 23 °C): δ 202.0 (t, $^2J_{PC}$ = 14 Hz, CO), 24.0 (virtual triplet, J = 9 Hz,[22] P*C*HCH$_3$), 20.1, 19.8 (each s, PCH*C*H$_3$), −13.4 (t, $^2J_{PC}$ = 7 Hz, RuCH$_3$). ^{31}P{^{1}H} NMR ($CDCl_3$, 23 °C): δ 36.6 (s).

X-ray Crystallographic Studies. Single crystals of **3a** and **5** suitable for X-ray diffraction study were obtained by recrystallization from Et_2O and toluene, respectively. The crystal of **4a** was grown by slow diffusion of the CH_2Cl_2 solution into MeOH at −20 °C. The crystal data and details of data collection and structure refinement are summarized in Table 2. Crystals were mounted on a glass fiber and fixed with an epoxy resin adhesive. All measurements were performed on a Rigaku AFC7R four-circle diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.710 69 Å). Unit cell dimensions were obtained from a least-squares refinement of the setting angles of automatically centered 25 reflections in the range 25° ≤ 2θ ≤ 30° for each crystal. Diffraction data were collected in the range 5.0 < 2θ < 55.0° using the ω−2θ scan technique at a scan rate of 16.0°/min in ω. The data were corrected for Lorentz and polarization effects, decay (based on three standard reflections monitored at every 150 reflection measurements), and absorption (empirical, based on azimuthal scans of three reflections).

All calculations were performed with the TEXSAN crystal structure analysis package provided by Rigaku Corp., Tokyo, Japan.[23] The scattering factors were taken from the International Tables for X-ray Crystallography.[24] The structure was solved by heavy-atom Patterson methods (PATTY) and expanded using Fourier techniques (DIRDIF94). The structures were refined by full-matrix least-squares with anisotropic thermal parameters for all non-hydrogen atoms. In the final cycles of refinement, hydrogen atoms with isotropic temperature factors (B_{iso} = 1.20$B_{bonded\ atom}$) were located at idealized positions (d(C−H) = 0.95 Å) and were included in calculations without refinement of their parameters.

Supporting Information Available: Details of the structure determinations of **3a**, **4a**, and **5**, including figures giving the atomic numbering schemes and tables of atomic coordinates, thermal parameters, and complete bond distances and angles (27 pages). Ordering information is given on any current masthead page.

OM980582H

(23) TEXSAN Structure Analysis Package, Molecular Structure Corp., 1985 and 1992.

(24) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, U.K., 1974; Vol. IV.